

Surfactant Drag Reduction Using Mixed Counterions

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I. Introduction

District cooling systems are used in many cities and large complexes such as airports in the U.S., Japan, and Korea. Typically water is cooled to 5°C at a central chilling station and circulated through the district until it heats up to 15°C. Then it is returned to the chiller to be re-cooled to 5°C. These systems have the advantage of eliminating the need for separate air conditioning in buildings in the district, increasing overall cooling efficiency, freeing up space in each building, and reducing maintenance costs in each building. The addition of ethylene glycol/water solutions increases the cooling capacity of the circulating fluid by allowing the cooling fluid to be cooled below 0°C.

While central chilling is more efficient than having each building have its own air conditioning, the energy to pump the fluid may be 15% of the total energy required. Reducing the pumping energy could have a significant impact on energy savings. Beyond the benefit of cutting operating costs for individual consumers, there is a global need to lower energy consumption and the effluent greenhouse gases produced by most electrical power generation plants.

The concept of using ethylene glycol/water solutions for district cooling and doubling the temperature range from 5°C to 15°C (ΔT of 10°C) to -5°C to 15°C (ΔT of 20°C) to increase the cooling capacity of the cooling system would reduce pumping energy requirements by about 50%. Use of effective drag reducing surfactant additives could reduce the pumping energy requirement by another 50% or a total of 75% reduction. However, the rate of heat transfer is also reduced by about the same amount as

the momentum transport. The heat transfer reduction must be overcome and this can be done by temporarily destroying the surfactant micelle structure network causing drag reduction and heat transfer reduction and having the micelles reassemble after leaving the heat exchanger.

Drag reduction is the lowering of friction losses associated with turbulent flow of fluid through pipes. Some cationic surfactant-counterion systems are effective drag reducers and can be utilized in aqueous recirculation systems to provide significant pumping energy savings. These surfactants form a micelle microstructure which causes drag reduction in straight pipe, but is broken up in regions of high stress such as in pumps. The micelles reassemble shortly after break-up when they reach a region of low shear and they again become drag reducing.

The addition of certain surfactant systems to ethylene glycol/water solutions in a district cooling system could also reduce the frictional drag and hence the energy required to pump the solution through the district. Unfortunately, highly effective drag reducers in water are often not as effective when added to ethylene glycol/water solutions. The primary goal of this research was to find cationic surfactant-counterion systems that would extend the effective temperature ranges for drag reduction in aqueous and in ethylene glycol/water solvents.

This study focused on using mixtures of counterions to improve the performance of a cationic surfactant over single counterions. Counterion mixtures were tested in both water and ethylene glycol/water solution. A particular focus was on finding mixtures with extended low temperature performance in both solvents. Previous studies for district heating systems utilized mixed cations in water. The mixed counterions were

found to extend drag reduction down to the lowest temperatures testable in our recirculation loop with only minor effects at high temperature when low concentrations of a C12 cationic was added to a C22 cationic. (1, 4, 5)

II. Literature and Theoretical Review

A. Surfactants

Surface-active agents or “surfactants” are molecules that consist of a polar head group and a nonpolar tail. The nonpolar tail consists of a long carbon chain. Surfactants are divided into four groups depending on the way the headgroup is charged. The headgroup can be: uncharged (non-ionic), positively charged (cationic), negatively charged (anionic) or with both a positive and negative charge on opposite sides (zwitterionic). A cationic surfactant was studied in this thesis.

B. Micelle Formation

When surfactants are present in aqueous solution, their behavior is dependent on concentration. At lowest concentrations in an open system, surfactants stay on the surface of the solution with their hydrophilic heads poked down into the water and their hydrophobic tails pointing up into the air. When there are too many surfactant molecules and not enough room for them on the surface, at a concentration called the critical micelle concentration (CMC_I), they will seek the lowest energy state in the form of micelles. The first micelle configuration to form is the spherical micelle, which allows the hydrophobic tails to avoid the water by clustering together at the center of the sphere. This formation is shown in Figure 1. The polar heads are on the surface of the sphere and interact with the polar water molecules to form hydrogen bonds. This configuration is present from the CMC_I to CMC_{II} or the first and second critical micelle concentrations, respectively.

Above the second critical micelle concentration, thread-like micelles will form. A cartoon view of a threadlike micelle is shown in Figure 2. Thread-like micelles are similar to spherical micelles in that their polar heads are still pointing outward, in contact

with the aqueous solution, and their hydrocarbon tails are still pointing inward creating a hydrophobic environment. The micelles are in the shape of a long cylinder, but can be of variable lengths and can contain branching.



Figure 1. Spherical micelle structure. (Ref 2)



Figure 2. Molecular structure of thread-like micelle. (Ref 2)

C. Drag Reduction

The pressure drop measured in the turbulent regime of a surfactant solution can be much lower than the pressure drop for the solvent at the same velocity. The frictional drag is reduced and the solution is drag reducing. The % drag reduction can be found by

comparing the $\Delta P/L$ measured with the measured or calculated value for the Newtonian solvent with no surfactant added.

The pressure drop measured in our system, ΔP , was used to calculate the drag reduction by determining the friction factor of the solution, f_{solution} . To obtain the friction factor of the solution, one must also know D , the diameter of the pipe; ρ , the density of the solution; v , the velocity of the solution in the pipe; and L , the length over which the pressure drop was measured. The following equation shows how these known values can be used to calculate the friction factor of the solution.

$$f_{\text{solution}} = \frac{D * \Delta P}{2 * L * \rho * v^2} \quad (1)$$

The percent drag reduction is then calculated using the difference between the friction factor of the solvent and the friction factor of the solution as in Equation 2. A solution is considered effective as a drag reducer if this value is greater than 50%.

$$\%DR = \frac{f_{\text{solvent}} - f_{\text{solution}}}{f_{\text{solvent}}} * 100\% \quad (2)$$

The von Karman equation, Equation 3, can be used to estimate the friction factor of the solvent.

$$\sqrt{1/f_{\text{solvent}}} = 4 * \log(\text{Re} * \sqrt{f_{\text{solvent}}}) - 0.4 \quad (3)$$

D. Temperature Effects

There is a clear effect of temperature on the formation of threadlike micelles and the resultant drag reducing ability of a surfactant in solution. At low temperatures, surfactants become less soluble, restricting their ability to form threadlike micelles. At high temperatures, surfactants also lose their drag reducing ability as threadlike micelles

become smaller. One or more organic counterions stabilize the micellar microstructures of cationic surfactants promoting drag reduction. The temperature range of effective drag reduction for a cationic surfactant is highly affected by the counterion or counterions used.

Chou found that a mixture of sodium salicylate and sodium 3-ethylbenzenesulfonate counterions provided greater stability to the micellar microstructures than single counterions (Ref 1) and increased the temperature range of effective drag reduction. The lower temperature limit became significantly lower with this mixture of counterions than with either counterion alone. The ratio of the counterions can be adjusted to maximize the effective temperature range for all counterion mixtures.

III. Experimental Procedures

A. Materials

Table 1 lists the surfactants and counterions used in this research.

Table 1. List of Materials

Chemical	Class	Purity, %	Source
Cetyltrimethylammonium chloride (CTAC)	Cationic Surfactant	99%	Nanjing Robiot
Sodium Salicylate (NaSal)	Salt	99%	Aldrich
3-Hydroxy-2-naphthoic acid (HSA)	Acid	98%	Aldrich
4-Ethylbenzenesulfonic acid (HEbs)	Acid	95%	Aldrich
Sodium Hydroxide (NaOH)	Base	-	Jenneile

i. Cetyltrimethylammonium chloride (CTAC)

CTAC is a cationic surfactant and which was used for all experiments in this thesis. The chemical structure of CTAC is given in Figure 3. The quaternary ammonium headgroup carries a positive charge and the chloride ion enters solution.

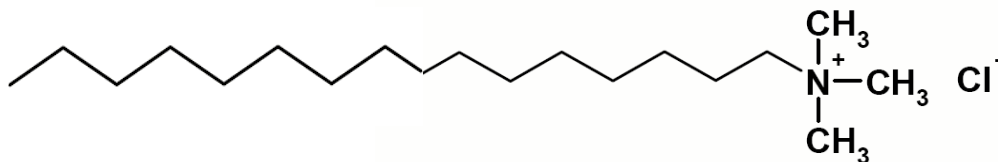


Figure 3. CTAC Chemical Structure

ii. Sodium Salicylate (NaSal)

The structure of NaSal is shown in Figure 4.

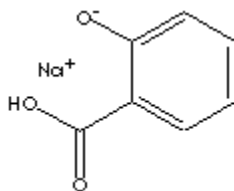


Figure 4. NaSal Chemical Structure

iii. Sodium Ethylbenzenesulfonate (NaEbs)

The structure of NaEbs is given in Figure 5. Sodium hydroxide was added to the 4-ethylbenzenesulfonic acid solution to produce this neutral salt.

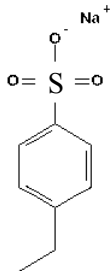


Figure 5. NaEbs Chemical Structure

vi. Sodium 3-Hydroxy-2-naphthoate (SHN)

The chemical structure of 3-hydroxy-2-naphthoic acid is shown in Figure 6. Sodium hydroxide was added to the acid solution to produce the neutral salt.

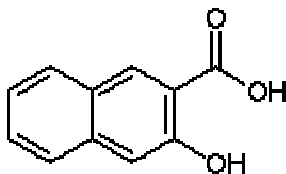


Figure 6. 3-Hydroxy-2-naphoic acid Structure

B. Preparation of Solutions

Approximately 20L of solution was prepared for each test. Dry chemicals were weighed in disposable dishes on the balance. Distilled water and ethylene glycol were measured in large beakers. Solutions were prepared in a 30L lined container with a free-standing electric mixer. Solutions were mixed for 8 hours and then allowed to rest for at least 8 hours before being loaded into the system. The pH of each solution was checked

before and after the mixing and resting period to insure consistency in our tests. If a particular solution was difficult to dissolve, a small space heater was mounted external to the bucket to heat the solution during the mixing and resting period. The solution was loaded into the drag reduction system through a funnel in the right tank. This funnel is labeled “Charge” in Figure 7.

The NaEbs and SHN counterions were purchased in their acid forms and the needed salts created in this step by the addition of NaOH to solution. The amount of NaOH added was controlled by a consistent pH and not done stoichiometrically.

C. Drag Reduction Measurement

A large recirculation loop was used to measure the drag reduction of each solution at various temperatures and Reynolds numbers. (2) A diagram of this system is shown in Figure 7 and a photo of the system in Figure 8. The entire system is composed of stainless steel parts to avoid corrosion and contamination of the solutions being tested. (2)

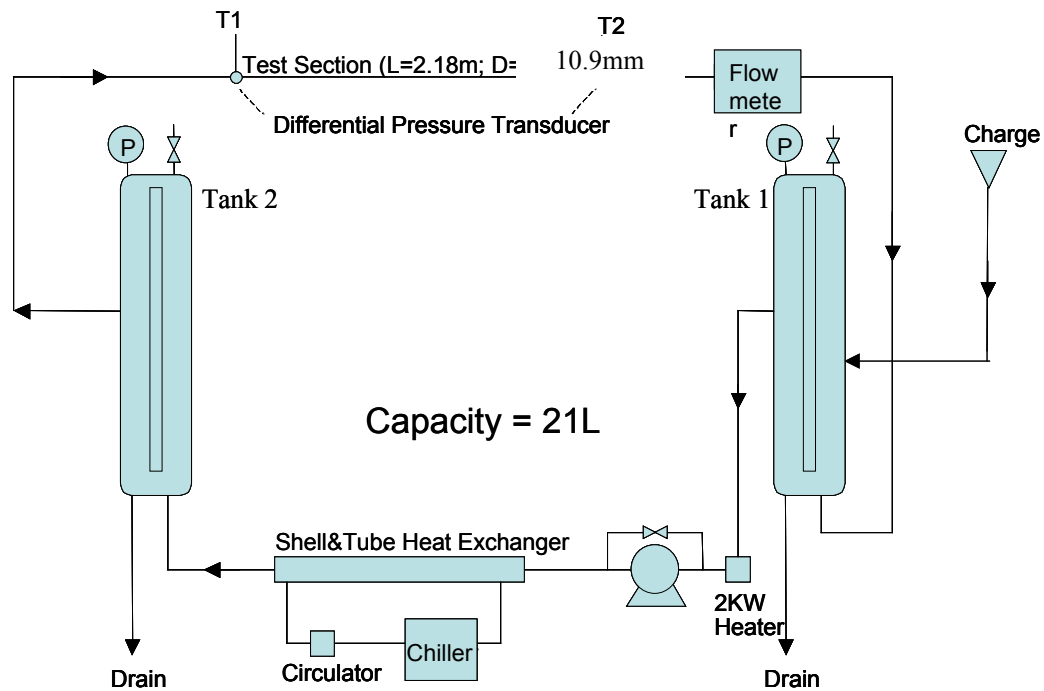


Figure 7: Drag Reduction System Components (Ref 2)

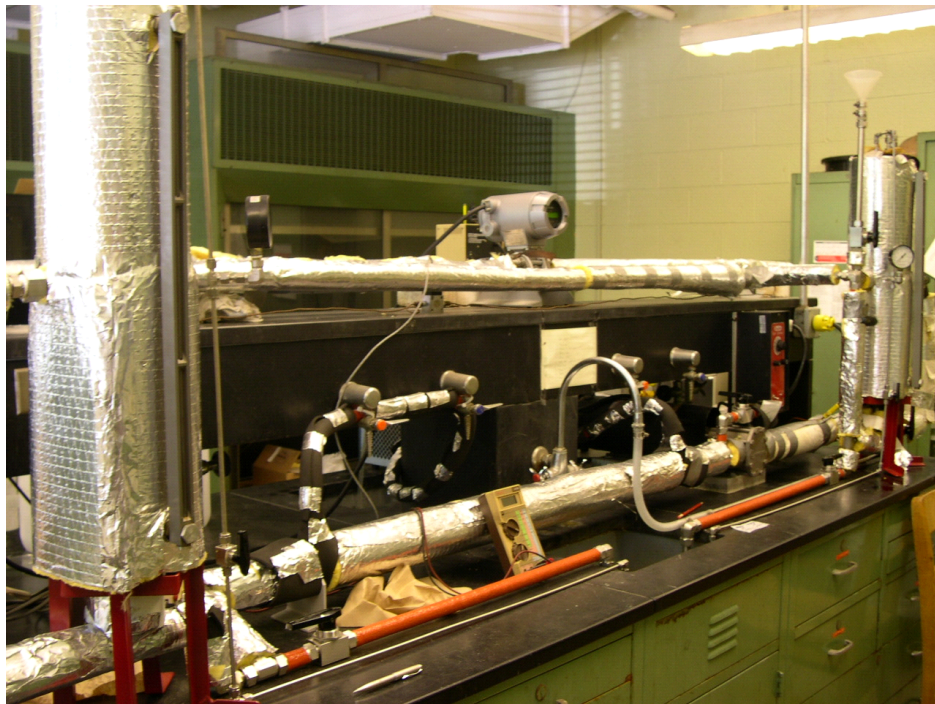


Figure 8: Drag reduction testing system photo(Ref 3)

The two tanks shown in Figure 7 are used to stabilize the system and avoid cavitation of the pump. The stabilization tanks also provide room for extra solution and temperature control. A small resistance heater is placed in line at the exit of the right tank before the pump. This heater is connected to a controller with a feedback loop. The operator enters a setpoint and the heater automatically turns on or off to maintain that temperature. The pump has a maximum flowrate of 30 gallons per minute, but can be run at various reduced flowrates by turning the knob controlling the variable speed drive.

After the solution leaves the pump, it flows through the test section. The test section length is approximately 2 meters of 0.5 inch stainless steel tubing (10.9mm internal diameter). This tube, though one of the highest points in the recirculation system, is kept full of liquid by the use of two air release valves on that section. These valves are at the position of T1 and T2 on Figure 7. A Rosemount Series 8700 magnetic flowmeter is located upstream of the test section. The flowmeter's digital display makes recording the flowrate convenient for the operator of the system.

All of the system that is in contact with liquid is heavily insulated to insure temperature consistency and to avoid energy loss. The temperature of the liquid in the system is measured by thermocouples at two separate locations. The output of one thermocouple, located near the bottom of the right tank, is used to control the heater for temperature control. Another thermocouple, located in the test section, gives a more reliable measure of the temperature in the test section and is displayed on a handheld device. Temperature stability for at least two minutes was required before values for flowrate and pressure drop were recorded.

The pressure drop over the length of the test section is measured by Validyne differential pressure transducers. The ΔP was recorded from a handheld display and reported in volts. The ΔP measurement is zeroed whenever the temperature of the system is changed. Before any data is taken, the flowmeter is turned off and the ΔP is read in a “zero flow” situation. This “zero flow” value is subtracted from all ΔP data taken in that temperature set.

A Polyscience Model KR-60A chiller is available in the testing loop for temperature control to allow measurement of drag reduction at temperatures below 20C. This chiller cools an ethylene glycol/water solution which is then pumped to a tube-in-tube heat exchanger to cool the surfactant solution. This coolant line is also heavily insulated to avoid energy loss. While the heater is controlled by a feedback loop which uses an inline thermocouple and a setpoint, the chiller is run manually by the operator of the test system. The chiller only operates in on and off modes.

D. Drag Reduction Calculations

The calculations needed to find the drag reduction were done in an Excel spreadsheet by entering the pressure drop, temperature, and flowrate. This spreadsheet template utilized equations (1), (2), and (3), and was created by previous students. The spreadsheet enabled quick and easy compilation of data into plots of percent drag reduction versus Reynolds number for each temperature tested.

E. Cryo-TEM imaging

Cryo-TEM imaging was conducted by Professor Yeshayahu Talmon and his group at the Technion-Israel Institute of Technology in Haifa, Israel. A photo of the

apparatus used for imaging is shown in Figure 9. They used cryo-transmission electron microscopy to provide images of the nanostructures of our complex fluids.

“Transmission electron microscopy (TEM) is one of the most useful techniques in the study of microstructured fluid systems. The technique involves ultra-fast cooling of thin liquid films, quenched from a controlled environment to vitrify the samples that are examined in the TEM at cryogenic temperatures.” (7)

Duplicate samples of the surfactant solutions were prepared at OSU and sent via FedEx to Professor Talmon. Used samples were not sent because of possible contamination from the recirculation loop system. The fresh solutions for shipping to Israel were prepared in the same way as the originals except for quantity.



Figure 9: Cryo-TEM imaging equipment (Ref 3)

IV. Results and Discussion

A. CTAC with Single Counterion

CTAC is the cationic surfactant used for this thesis. All solutions tested incorporated CTAC at a concentration of 5mM.

i. Sodium Salicylate (NaSal)

Negatively charged organic counterions associate strongly with the positive headgroup dispersing the positive charges and enabling the CTA^+ moiety to form micelles. The phenyl group penetrates into the micelle as shown by NMR results (6). A baseline for the counterion effect with CTAC was set using only sodium salicylate.

The counterion, NaSal, was tested at 12.5mM, a molar ratio of $\xi = 2.5$. This solution was drag reducing from 15-75°C with a maximum drag reduction of 82% at 65°C as shown in Figure 10.

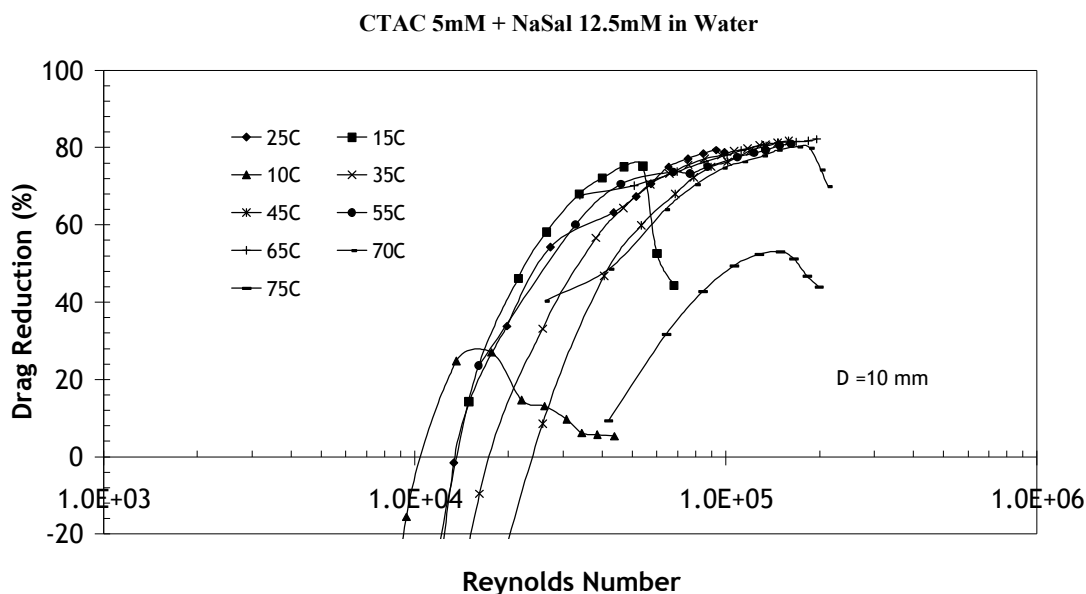


Figure 10. Drag Reduction with 12.5mM NaSal in water

The same concentrations of CTAC and NaSal were then tested in a solution of 20% ethylene glycol/water. Addition of ethylene glycol to water had a negative effect on the drag reducing ability of the solution. First, the solution had a much lower effective drag reducing temperature range (15-40°C). Second, the maximum drag reduction was reduced to 71% at 35°C. Figure 11 shows these results.

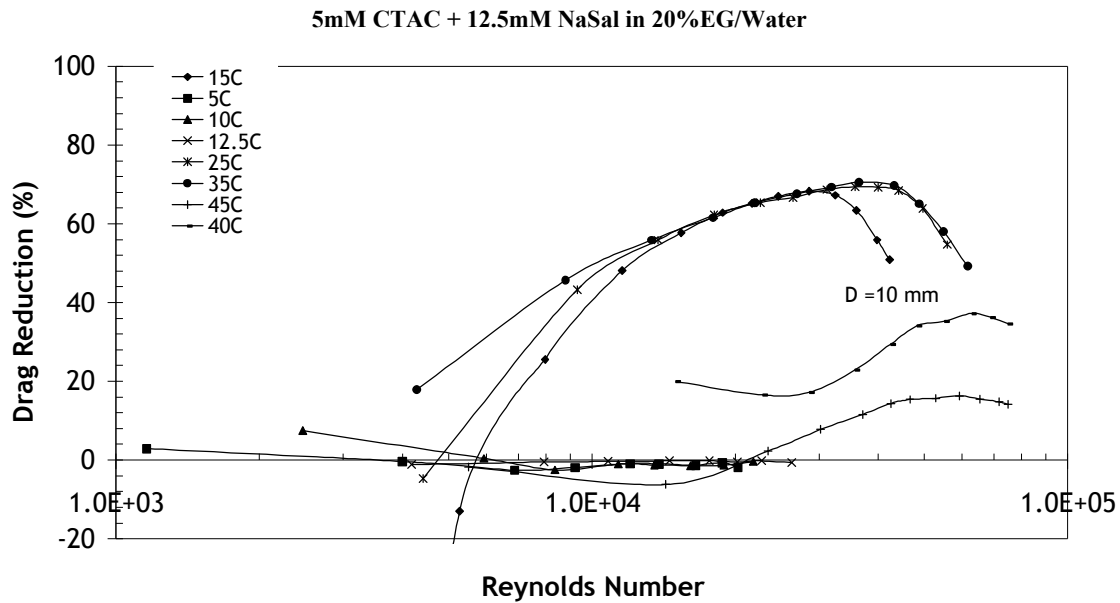


Figure 11. Drag Reduction with 12.5mM NaSal in 20% EG/water

ii. Sodium 3-Hydroxy-2-naphthoate

Sodium 3-Hydroxy-2-naphthoate (SHN) was the second counterion tested. A solution of 5mM CTAC with 12.5mM SHN in water was run in the system. SHN was inferior to NaSal as a drag reducer. The effective drag reducing range was only ten degrees (85-95°C) and the maximum drag reduction observed was 66% as shown in Figure 12.

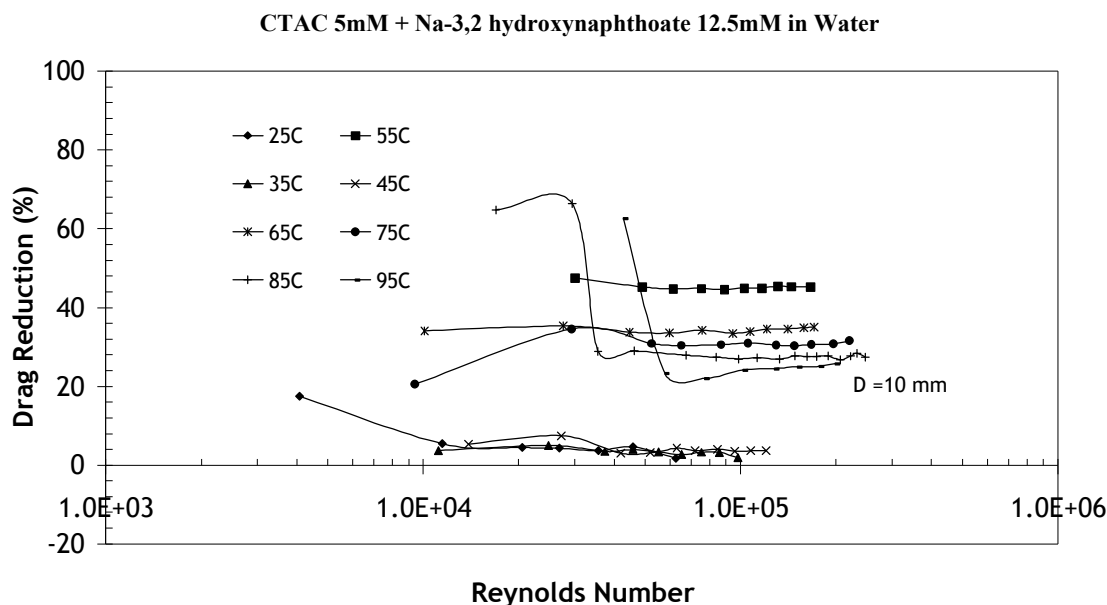


Figure 12. Drag Reduction with 12.5mM SHN in water

SHN was not tested in 20% ethylene glycol/water solution because it was so weakly drag reducing in water.

B. CTAC with Mixed Counterions

5mM CTAC solutions were then tested with mixtures of the two counterions. At an overall counterion concentration of 12.5 mM, but with varying ratios of the two counterions. This testing was an extension of the work presented by Chou in his 1991 dissertation in which he found aqueous solutions of 5mM CTAC with certain ratios of NaEbs and NaSal to be drag reducing to 2°C.

i. Sodium Salicylate and Sodium Ethylbenzenesulfonate (NaEbs)

This combination of counterions was originally tested by Chou who found that mixtures of the two counterions lowered the effective drag reduction temperature down to the lowest temperature obtainable in his system, 2°C. 5mM CTAC solutions with a 12.5mM mixture of NaEbs and NaSal were drag reducing to the lowest attainable

temperature from 0.2 through 0.5 mole fraction NaEbs. In our attempts to lower the temperature limit below 2°C, NaSal-NaEbs/CTAC systems were also tested in 20% ethylene glycol/water.

To confirm Chou's results, 5mM CTAC and 12.5mM counterion (0.2 mol fraction NaEbs and 0.8 mol fraction NaSal) systems in water were tested. The results were similar to those reported by Chou and are shown in Figure 13. He found this solution to be drag reducing down to 2°C.

Several ratios of NaEbs to NaSal (total of 12.5mM) in ethylene glycol solution with 5mM CTAC were also tested. The results for 60% NaEbs and 40% NaSal in EG/water are shown in Figure 15 and the results for all ratios are shown in Figure 14.

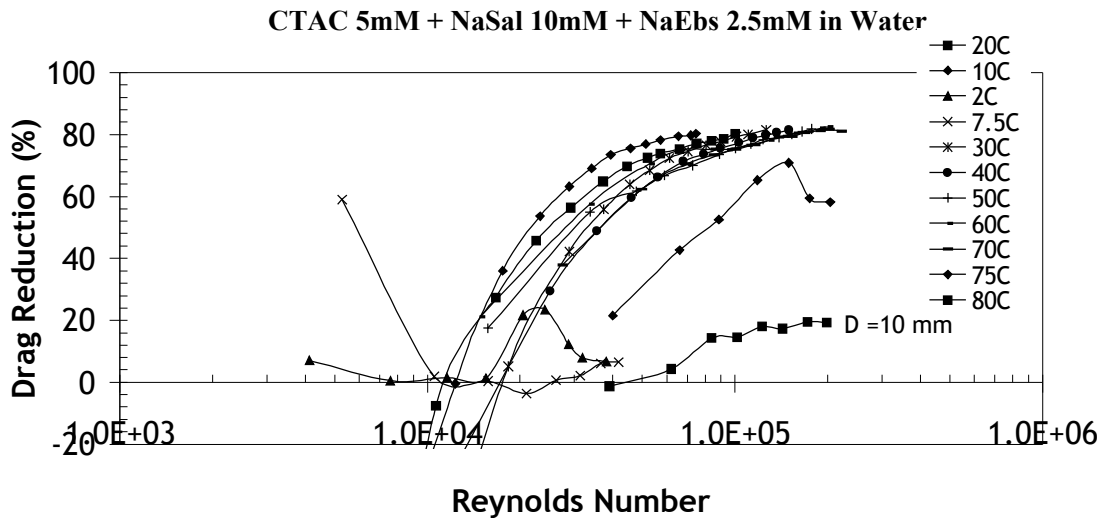


Figure 13. Drag Reduction with 20% NaEbs and 80% NaSal in water

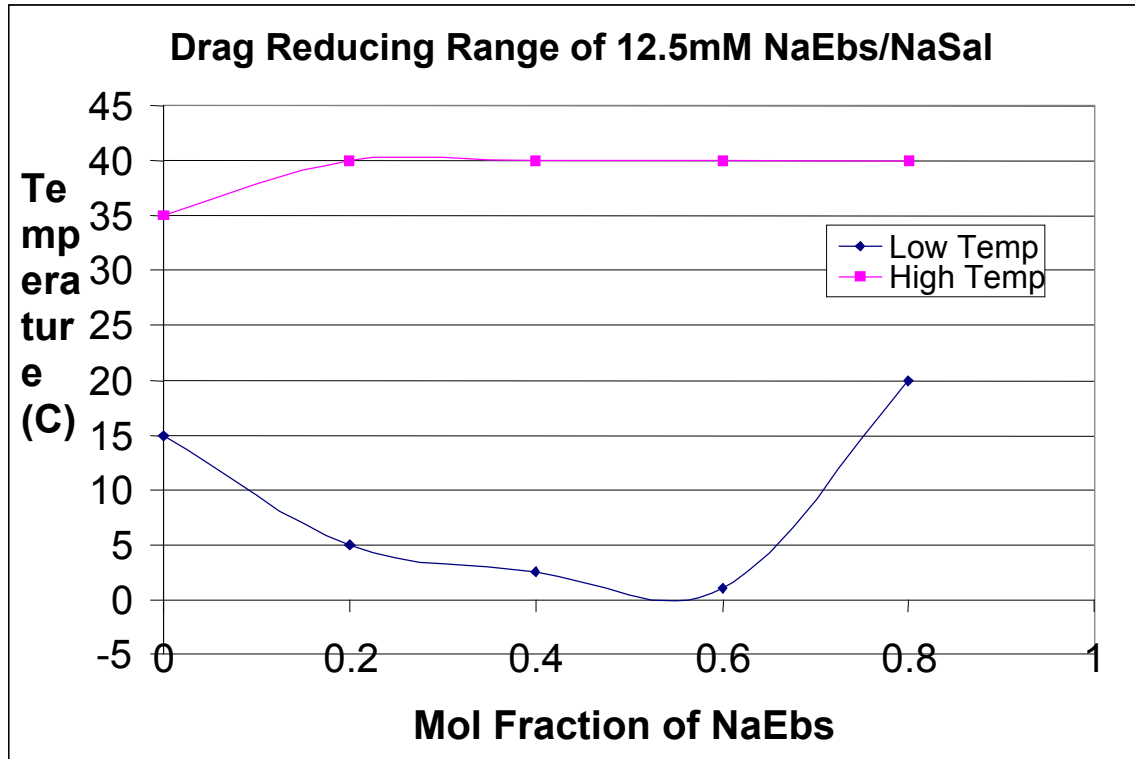


Figure 14. Effective Temperature range of NaEbs/NaSal in 20% EG/water

The drag reductions for the ratios versus Reynolds number at all temperatures tested in EG/water are plotted in Figure 14. The maximum drag reduction was 69%. However, the addition of 20% ethylene glycol to the solution was not beneficial in lowering the lower temperature limit since drag reduction below 0°C could not be reached.

The upper “High Temp” line shows the upper temperature limit of drag reduction for each mixture ratio tested. The lower “Low Temp” line shows the lower temperature limit of drag reduction and the temperature range over which drag reduction is greater than 50% lies between the two lines. While the upper temperature limit is not affected much by the counterion ratios, the lower temperature limit is dramatically decreased

approaching 0°C for 40-60% NaEbs, with 60% effective drag reduction down to about 2°C.

Extending the low temperature limit for effective drag reduction is a very interesting result. It is not completely understood why using two counterions gives more effective drag reduction than using either of them alone, but it is probably related to the packing of the cationic surfactant with mixed counterion molecules in the threadlike micelles.

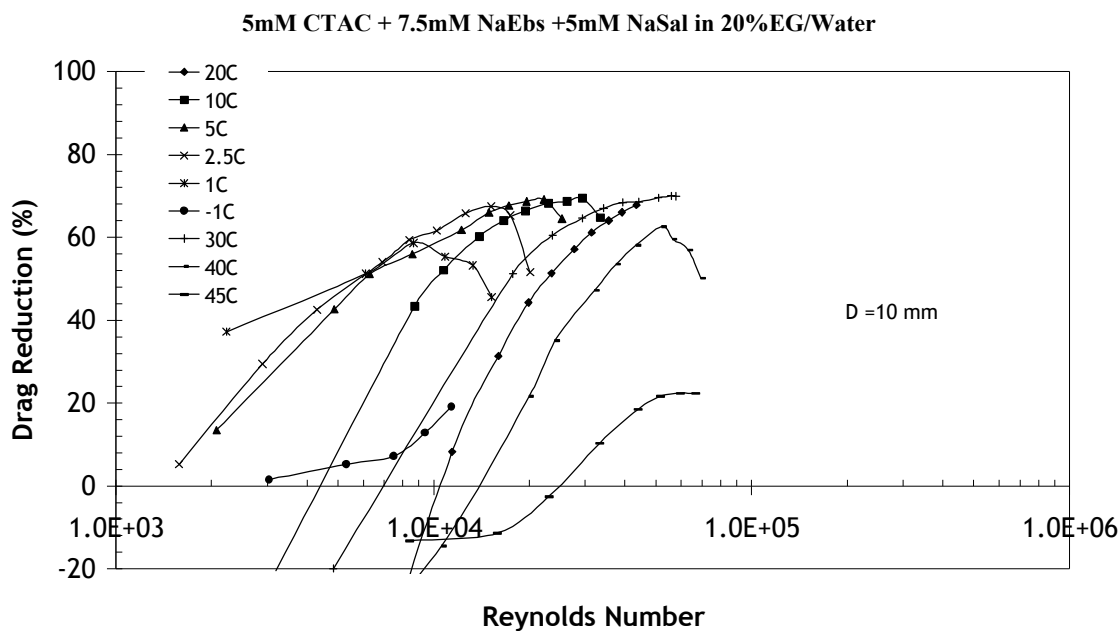


Figure 15. Drag Reduction with 60% NaEbs/40% NaSal

ii. Sodium Salicylate and Sodium 3-Hydroxy-2-naphthoate

Similar behavior was observed when a second pair of counterions, sodium salicylate and sodium 3-hydroxy-2-naphthoate, were tested at different ratios. Table 2 summarizes all the ratios tested.

Table 2. Summary of NaSal/SHN Performance

Summary of Counterion Ratios in Water and 20%EG/Water						
Concentration (mM)		In Water		In 20% EG/Water		
Na-Sal %	Na-Sal	SHN	Significant Temp range (°C)	Maximum % DR	Significant Temp range (°C)	Maximum % DR
0%	0	12.5	85 - 95	66% (85°C)	-	-
25%	3.125	9.375	30 - 35	69% (30°C)	-	-
50%	6.25	6.25	25 - 75	70% (75°C)	-	-
75%	9.375	3.125	3 - 95 *	81% (55°C)	5 - 65	75% (55°C)
87.50%	10.94	1.56	2 - 95 *	81% (75°C)	2 - 55	73% (45°C)
100%	12.5	0	15 - 75	82% (65°C)	15 - 40	71% (35°C)

*Effective Drag reducer over entire range of temperatures obtainable in system.

The trends in effective temperature range of these solutions are best seen in Figure 16.

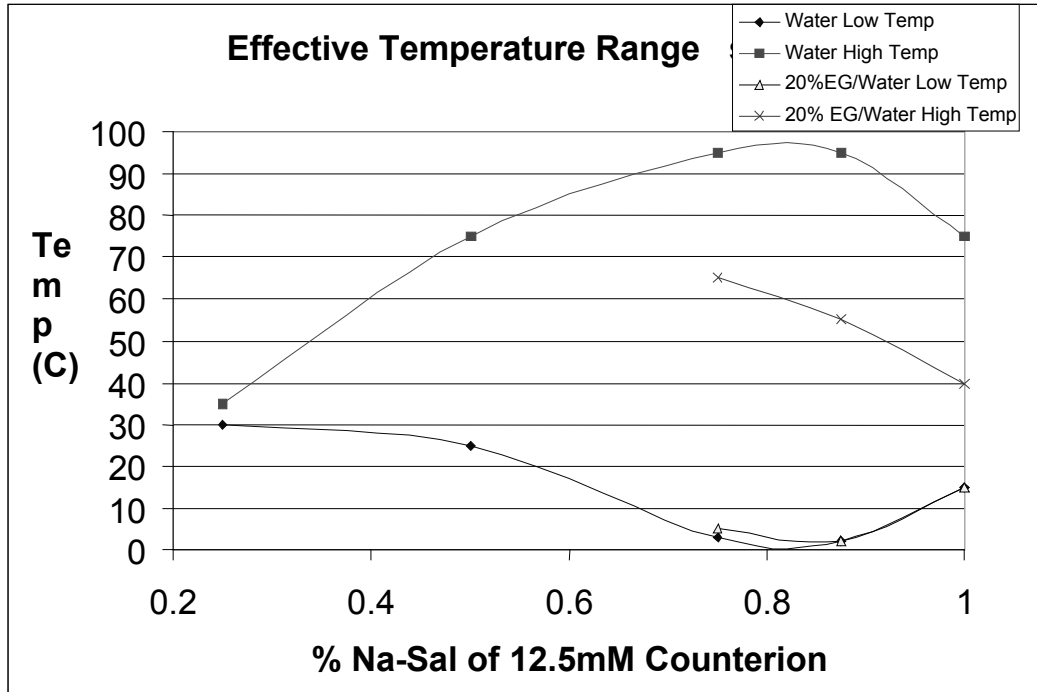


Figure 16. Effective Temperature Range of NaSal/SHN in water and 20% EG/water

Addition of minor amounts of SHN raised the high temperature limit and reduced the low temperature limit for both water and EG/water solutions.

The maximum drag reducing range observed was at 75% NaSal and 25% SHN in EG/water and 9.375mM NaSal and 3.125mM SHN in water. The drag reduction plot for the latter solution is shown in Figure 17. This solution was drag reducing over the entire temperature range which could be tested in our system, 3-95°C, and also has very high percent drag reduction over a wide range of Reynolds numbers. Thus, this system would be suitable for both conventional aqueous district cooling systems and district heating systems most of which operate below 95°C. The maximum drag reduction of 81% was observed at 55°C; however, as evident in Figure 17, the % drag reduction was around 80% at many temperatures.

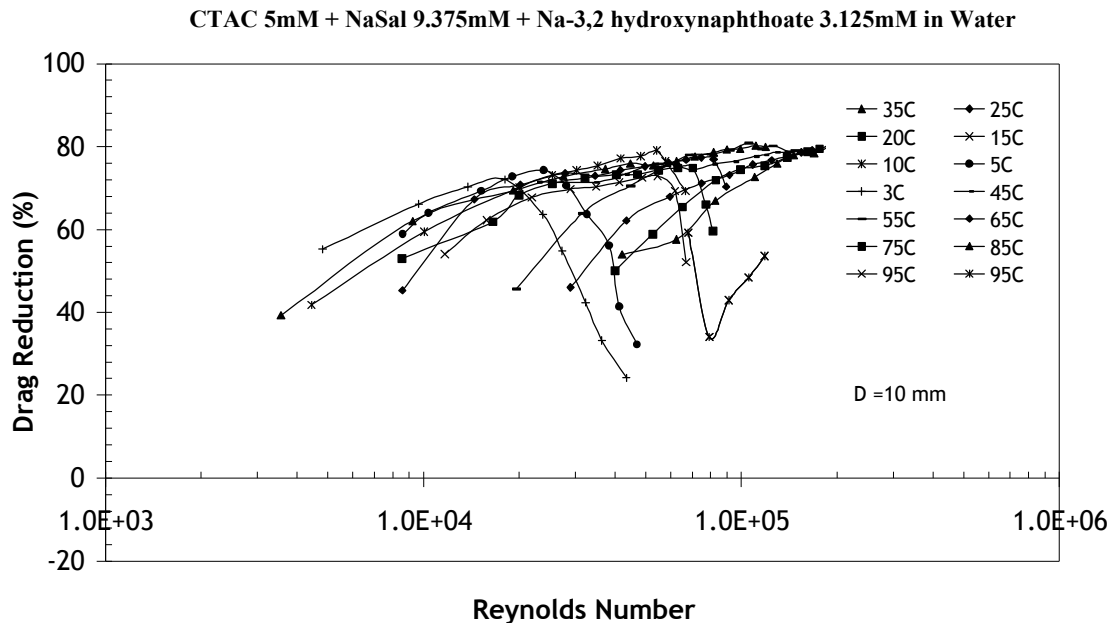


Figure 17. Drag Reduction with 75% NaSal/ 25% SHN in water

The addition of ethylene glycol hurt the performance of the solutions at every temperature tested. It both decreased the maximum drag reduction and decreased the temperature range. The lower limit appears unaffected while the upper temperature limit dropped an average of 35°C from the water solution when 20% ethylene glycol was added.

A somewhat higher ratio than for water, 0.875 mol fraction NaSal, gives the optimal performance in 20% ethylene glycol. Figure 18 shows drag reduction data for the 87.5%Na-Sal/12.5% Na-3,2-hydroxynaphthoate solution in 20% ethylene glycol/water. This solution showed considerable drag reduction at the lowest temperature observed in this study. It reached 42% DR at 0°C. This solution appears to be near the optimum counterion ratio for the low-end temperature limit of this pair of counterions in 20% ethylene glycol/water.

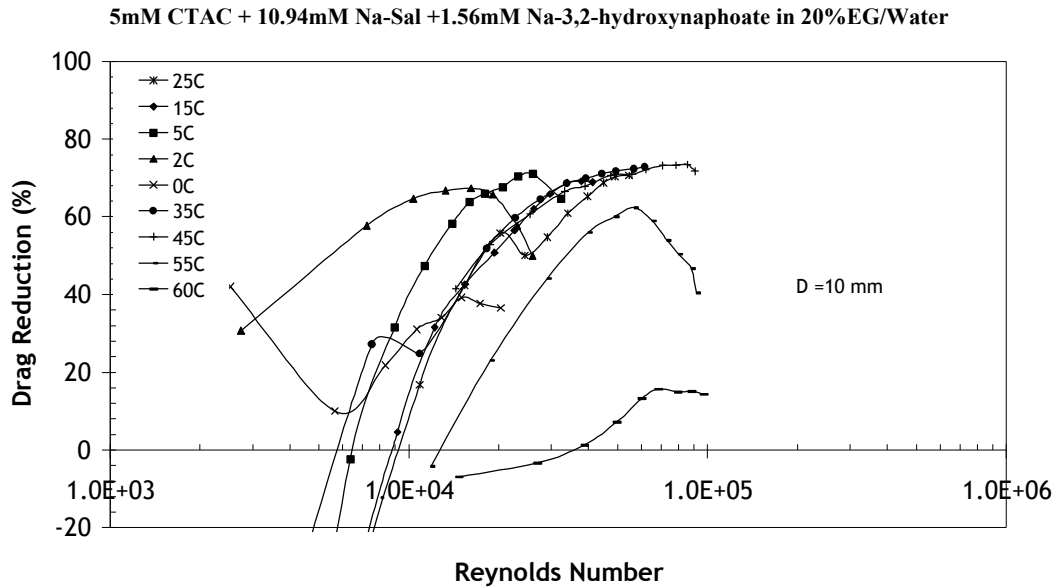


Figure 18. Drag Reduction with 88% NaSal/ 12% SHN in 20%EG/water

Because the best ratios in 20% EG/water did not give 50% drag reduction below the freezing point, no more solutions were tested.

CryoTEM imaging of the 50% NaSal and 50% SHN system in water was conducted at 40°C by Professor Talmon's group in Israel. This solution was found to be drag reducing at that temperature. This image shows vesicles in the quiescent state as shown in Figure 19. While threadlike microstructures are normally observed for drag reducing solutions, this unusual vesicle microstructure for a drag reducing solution was observed previously (Zhang et al). Zhang showed that in certain drag reducing systems, vesicles are observed in the quiescent state, but, under shear, the microstructures transform to threadlike micelles which lead to drag reducing behavior.

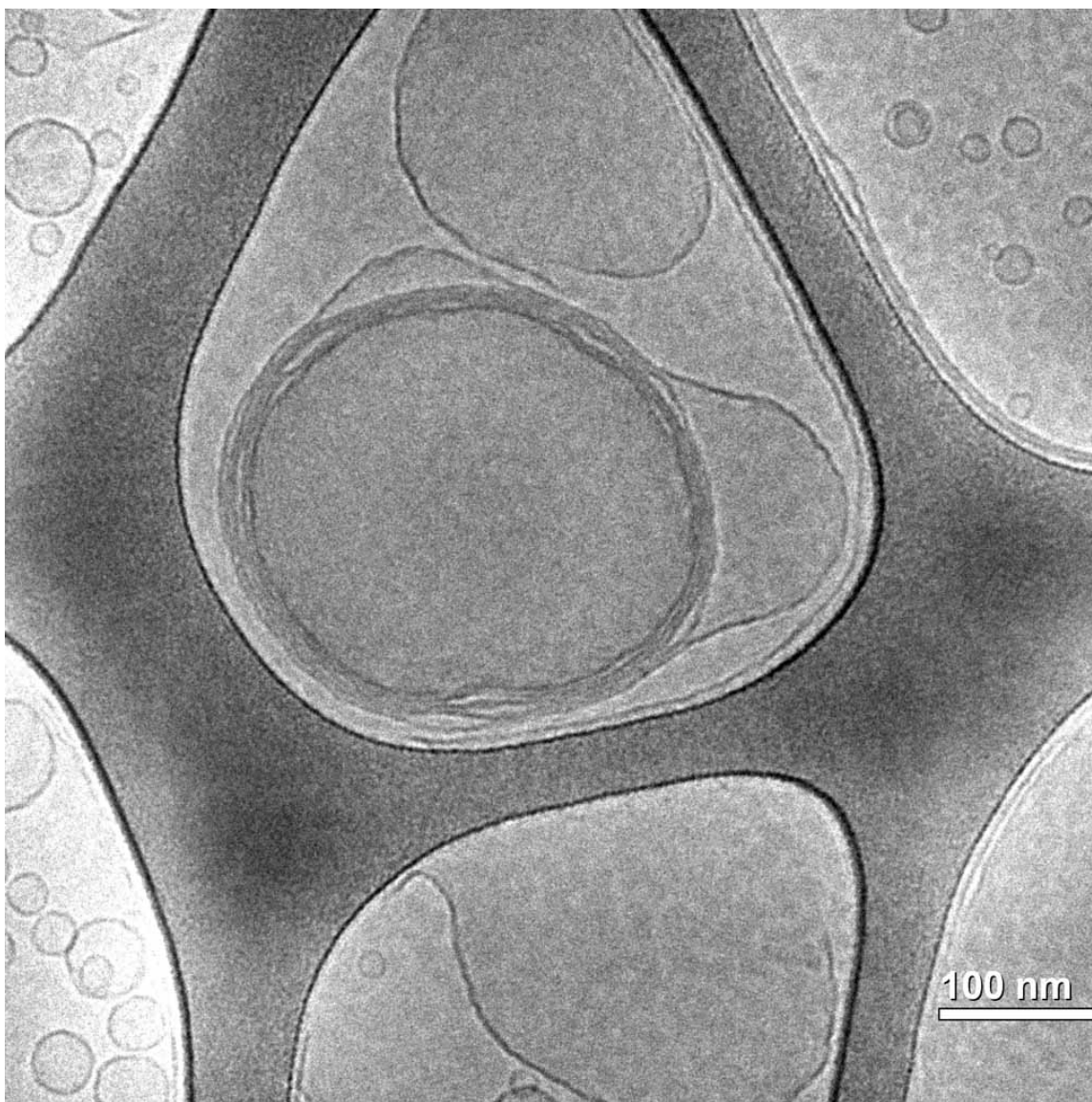


Figure 19. CryoTEM image of 50% NaSal and 50% SHN in water at 40°C

Professor Talmon's group also produced a CryoTEM image of 10.9mM NaSal and 1.6mM SHN in 20%EG/water solution. This imaging was done at 40°C, above the middle of the drag-reducing temperature range. The threadlike micelles clearly visible in Figure 20 are typical of what is expected of a drag-reducing solution. The white arrow in the figure points to branching in the threadlike micelles. The low contrast in the image is due to the ethylene glycol solvent used.

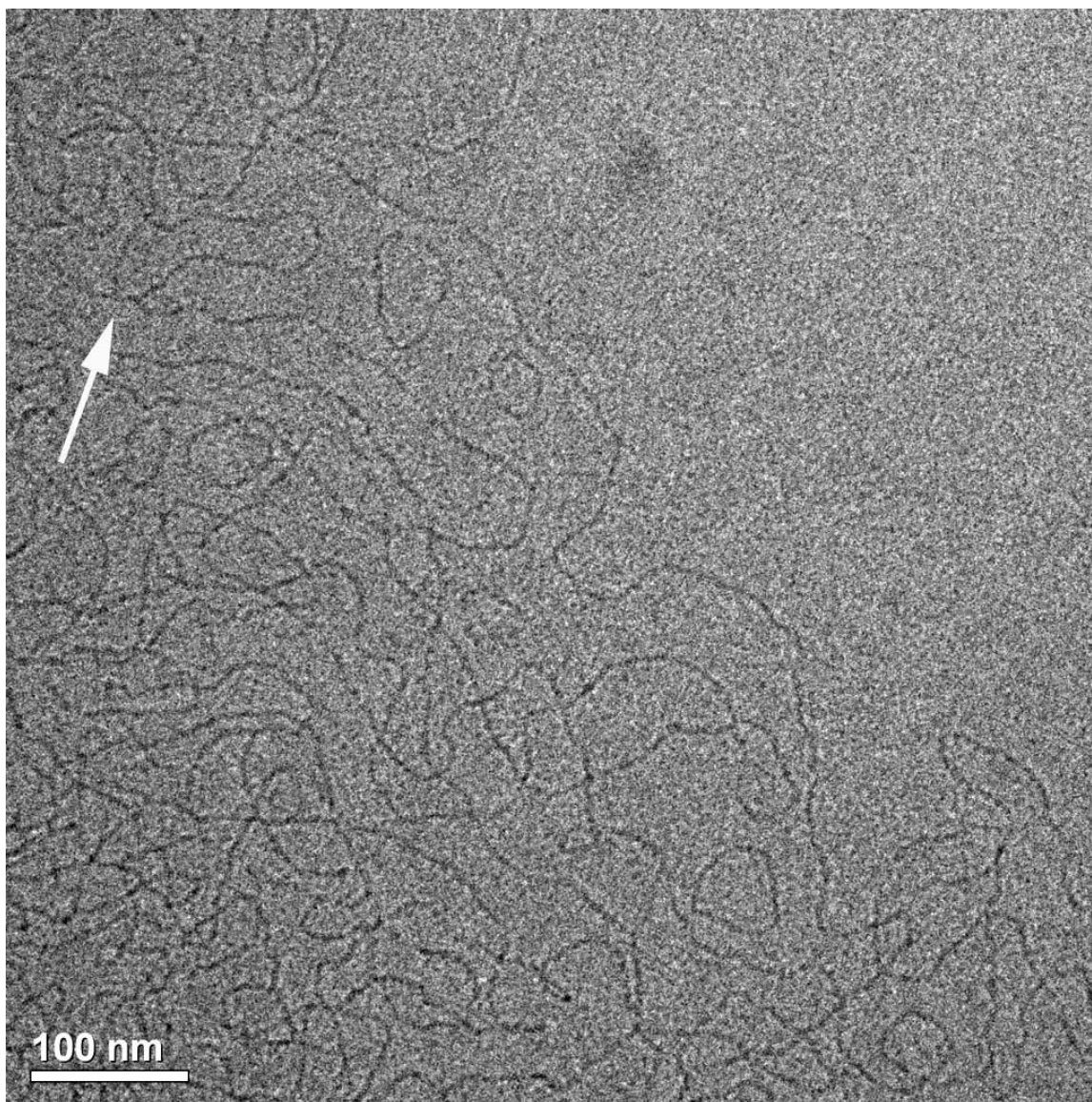


Figure 20. CryoTEM image of 10.9mM NaSal and 1.6mM SHN in 20%EG/water at 40°C

Conclusions

1. Certain ratios of two counterions result in increased maximum drag reduction and extended effective temperature range compared with either counterion at the same total counterion concentration. The aqueous system of 75% NaSal and 25% SHN gave effective drag reduction over the entire temperature range of our testing system (2-95°C). This surfactant system is a candidate for use in conventional aqueous district cooling and in aqueous district heating systems.
2. Surfactant solutions with mixed counterions in 20% EG/water show the same pattern of behavior as in water but with less effective drag reduction. Lower effective upper temperatures and lower maximum drag reductions were found in the 20% EG/water solvent.
3. The Cryo-TEM images of surfactant microstructures are consistent with the observed drag reducing behavior.

References

1. Chou, L.C., *Drag Reducing Cationic Surfactant Solutions for District Heating and Cooling Systems*, Ph.D. Dissertation, The Ohio State University, Columbus 1991.
2. Zhang, Ying, *Correlations among Surfactant Drag Reduction, Additive Chemical Structures, Rheological Properties and Microstructures in Water and Water/Co-solvent Systems*, Ph.D. Dissertation, The Ohio State University, Columbus 2005.
3. Ge, Wu, *Surfactant Turbulent Drag Reduction in an Enclosed Rotating Disk Apparatus*, Presented at MUFMECH 2006, April 2006.
4. Lin et al., *Experimental studies on drag reduction and rheology of mixed cationic surfactants with different alkyl chain lengths*, Rheol Acta (2000) 39: 354-359.
5. Lin, Zhiqing, *The Effect of Chemical Structures of Cationic Surfactants or Counterions on Solution Drag Reduction Effectiveness, Rheology, and Micellar Microstructures*, Ph.D. Dissertation, The Ohio State University, Columbus 2000.
6. Smith et al., *Measurement of the orientational binding of counterions by nuclear magnetic resonance measurements to predict drag reduction in cationic surfactant micelle solutions*, J. Rheol. (1994) 38(1): 73-83.

7. Talmon, Y., *Digital Imaging Cryogenic-Temperature Transmission Electron Microscopy (Cryo-TEM) of soft matter*, Department of Chemical Engineering, Technion- Israel Institute of Technology, Haifa.
<http://www.technion.ac.il/technion/materials/ism/Docs/2001/Ishi.pdf>
8. Zheng et al., *Cryo-TEM Imaging the Flow-Induced Transition from Vesicles to Threadlike Micelles*, Phys Chem B, (2000) 104(22): 5263-5271.
9. Ge, Wu, Personal Communication, May 15, 2006.

Appendix I. New Heat Transfer System Construction

A good portion of my time has been spent helping to design and construct a new system to measure heat transfer in surfactant solutions. This system is largely a reconstruction of one that already existed. The original system was designed to test heat transfer in surfactant solutions at temperatures higher than 20°C. The intended application of the new system is for testing district heating systems. The new system we are constructing will test surfactant solutions at low temperatures and be applicable to district cooling systems. The system under construction is located in the 3rd floor unit operations area of Koffolt Labs.

It is known that surfactant drag reduction is accompanied by a reduction in heat transfer. This is deleterious for the application of these solutions to district heating and cooling systems. One solution to this problem is to install a destructive device ahead of the heat exchanger to temporarily break the micelle microstructures. The new heat transfer system is designed to have removable tubing sections with different internal structures (i.e. honeycomb) to test different devices.

The new low temperature system presented many challenges over the original. First, the new system needed to reach much higher pressures (maximum 200 psi) than the original to operate. The old system utilized many pipe fittings which had to be eliminated because of this high pressure requirement. Also, the fittings connected to the tanks had to be welded to make them safe at high pressures. Second, the new system required reduced pressure drop around the loop than the old to accommodate the high viscosity of EG/water at low temperatures. Pressure drop was minimized in the new

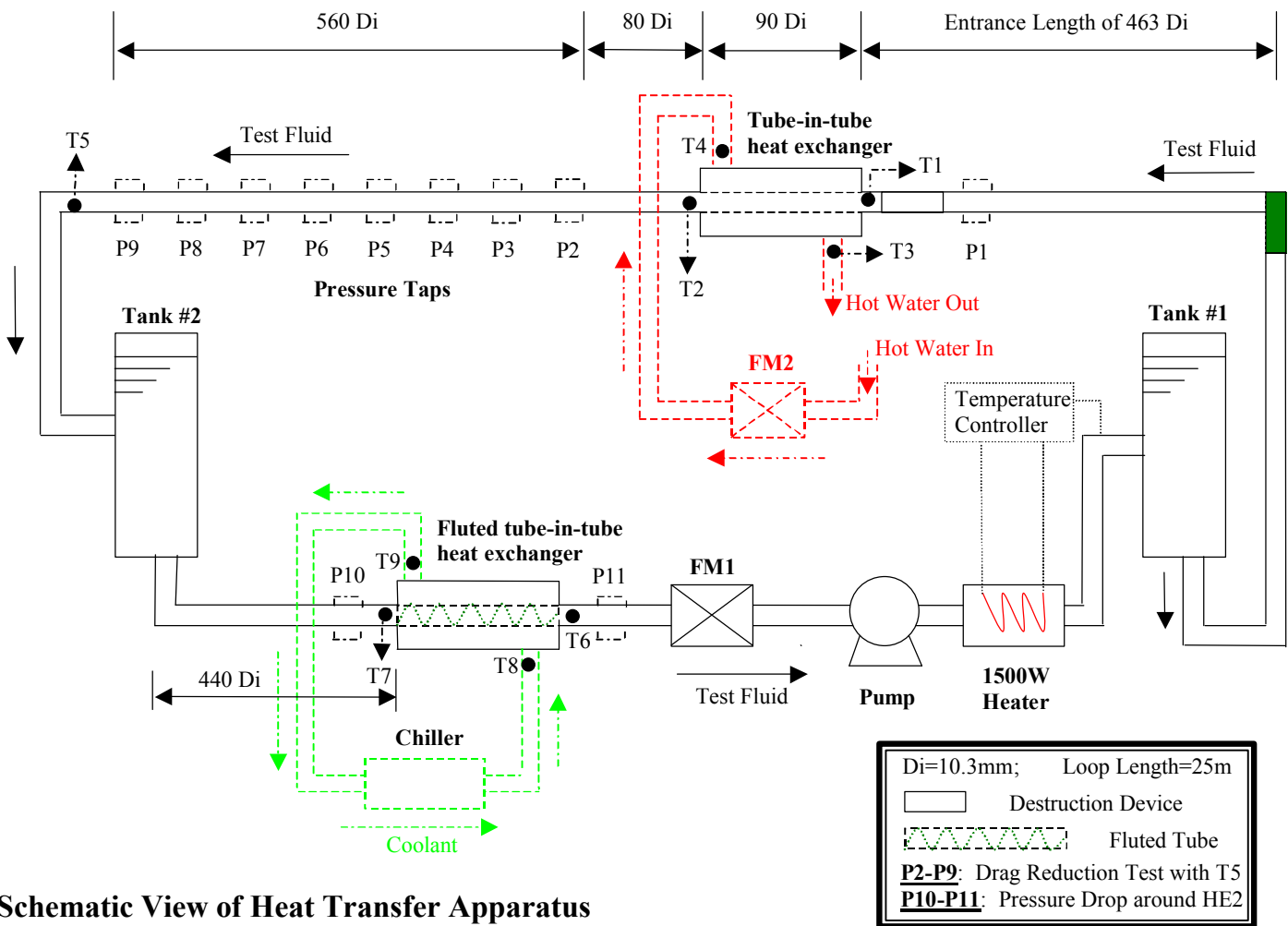
system by shortening pipe lengths, minimizing elbows, and using large radii bends rather than fittings that had sharp bends.

The most significant challenge ahead will be adapting the existing chiller to work in our new system and reach the low temperatures at which we want to test. Calculations were done (Ref 8) to show that to test a 20% EG/water solution at 0°C would require a 4kW chiller. This is assuming a maximum fluid velocity of 6m/s (maximum $Re = 19000$). The chiller we possess is over double that capacity.

My contributions to this project have been predominately researching and ordering materials and pipe fitting. Before construction began, I gathered the components of the system (both new and those salvaged from the old system) and ordered the tube fittings needed for construction. In parallel, work on the data acquisition system began with its installation in a home-made housing. Significant changes to the original support system for tubing, equipment, and tanks had to be made during construction. The tanks were installed inside steel supports and all tubing was insulated then locked into hangers bolted to steel supports. All pressure taps and thermocouples are installed. Delays, including replacement of low-pressure fittings, the welding of the steel tanks, and the writing of this thesis, have us still in the construction phase of this project.

Calculations were done (Ref 8) before construction began to ensure that this new system could operate in the temperature and flowrate ranges of most interest to us. The maximum absolute pressure in the loop is 200psi. A solution of 20% EG/water at 0°C can reach a maximum Re of 19000. Higher Re values can be reached in solutions with either higher temperature or lower viscosity (i.e. water).

Appendix II is the schematic of this new system.



Schematic View of Heat Transfer Apparatus